

AD-A152 734

MEASUREMENT OF FRANCK-CONDON FACTORS FOR THE $V'=0$
PROGRESSION IN THE B-X S. (U) ARMY BALLISTIC RESEARCH
LAB ABERDEEN PROVING GROUND MD W R ANDERSON ET AL.
DEC 84 BRL-TR-2627 SBI-AD-F300 598

1/1

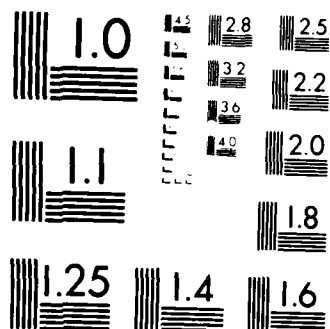
UNCLASSIFIED

F/G 7/2

NL

				END									

NOTE: FILMED
DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

B
R
L

AD-A152 734

AD

(2)

TECHNICAL REPORT BRL-TR-2627

MEASUREMENT OF FRANCK-CONDON FACTORS
FOR THE $V'=0$ PROGRESSION IN
THE B-X SYSTEM OF PO

William R. Anderson
Steven W. Bunte
Anthony J. Kotlar

December 1984

DTIC
ELECTE
APR 16 1985
S B

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

US ARMY BALLISTIC RESEARCH LABORATORY
ABERDEEN PROVING GROUND, MARYLAND

DTIC FILE COPY

Destroy this report when it is no longer needed.
Do not return it to the originator.

Additional copies of this report may be obtained
from the National Technical Information Service,
U. S. Department of Commerce, Springfield, Virginia
22161.

The findings in this report are not to be construed as an official
Department of the Army position, unless so designated by other
authorized documents.

The use of trade names or manufacturers' names in this report
does not constitute indorsement of any commercial product.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER TECHNICAL REPORT BRL-TR-2627	2. GOVT ACCESSION NO. AD-A152713	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) MEASUREMENT OF FRANCK-CONDON FACTORS FOR THE $v'=0$ PROGRESSION IN THE B-X SYSTEM OF PO		5. TYPE OF REPORT & PERIOD COVERED Final
7. AUTHOR(s) William R. Anderson Steven W. Bunte Anthony J. Kotlar		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Army Ballistic Research Laboratory ATTN: AMXBR-IBD Aberdeen Proving Ground, MD 21005-5066		8. CONTRACT OR GRANT NUMBER(s)
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Army Ballistic Research Laboratory ATTN: AMXBR-OD-ST Aberdeen Proving Ground, MD 21005-5066		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 1L161102AH43
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE December 1984
		13. NUMBER OF PAGES 29
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION DOWNGRADING SCHEDULE NA
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release; Distribution Unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) PO Radical Laser Excited Fluorescence Franck-Condon Factors Organophosphonate Esters		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) gkl Laser Fluorescence of PO produced in a microwave discharge through organophosphonate esters has been studied. The fluorescence was pumped in the B doublet sigma plus - X doublet pi 3250 Angstrom system. Relative intensities of fluorescence for the v' prime equals zero progression were measured. These intensities were used to derive Franck-Condon factors for the v' prime equals zero progression.		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

TABLE OF CONTENTS

	<u>PAGE</u>
I. INTRODUCTION.....	5
II. EXPERIMENTAL.....	6
III. RESULTS AND DISCUSSION.....	6
IV. CONCLUSIONS.....	18
ACKNOWLEDGEMENTS.....	19
REFERENCES.....	20
DISTRIBUTION LIST.....	23

APR 16 1985

Accession For

NINE COPIES
[]
[]
[]
[]

[] by Code9
and/or
[]

A-1

I. INTRODUCTION

Electronic spectra of the PO radical have been known and studied for over 50 years.¹ Studies of the transition between the two lowest-lying electronic states, the $B^2\Sigma^+ + X^2\Pi$ 3250Å system, have concerned rotational²⁻⁵ and vibrational^{3,4} analyses and B state perturbations.^{3,5} More recent investigations have reported the laser excited fluorescence (LEF)⁶ and multiphoton ionization spectra.^{7,8} Our interest in this radical results from its involvement in several possible fragmentation detection schemes for nerve agents since their chemical structure is centered around a PO double bond. In the present work, LEF of the B-X system was further studied. A more detailed account of the procedures and results is given than has previously appeared.⁹ The PO was produced in a microwave discharge through two chemicals

¹References to earliest work may be found in Spectroscopic Data, Heteronuclear Diatomic Molecules, Vol. I, ed. S.N. Suchard, IFI/Plenum Data Company, NY, 1975. A compilation of papers from 1955 to 1979 is available in K.P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure, IV. Constants of Diatomic Molecules, Van Nostrand Reinhold, Co., NY, 1979.

²N.L. Singh, "Rotational Analysis of the β Bands of Phosphorus Monoxide," Can. J. Phys., Vol. 37, p. 136, 1959.

^{3a}R.D. Verma and S.R. Singhal, "New Results on the $B^2\Sigma^+$, $b^4\Sigma^-$ and $X^2\Pi$ States of PO," Can. J. Phys., Vol. 53, p.411, 1975.

^bS.R. Singhal, "High Resolution Study of the Spectral Region 3000Å - 3900Å of the PO Molecule," Ph. D. Thesis, University of New Brunswick, Fredericton, New Brunswick, Canada, 1973.

⁴C. Couet, N. Tuan Anh, B. Coquart and H. Guenebaut, "Contribution A L'Etude Des Systemes Electroniques du Radical PO. 3^e Partie: Le Systeme β (transition $B^2\Sigma^+ - X^2\Pi$), J. Chim. Phys., Vol. 65, p. 217, 1968.

^{5a}S.B. Rai, D.K. Rai, and K.N. Upadhyaya, "Analysis of Some Bands of the β System of PO," J. Phys. B: Atom. Molec. Phys., Vol. 5, p. 1038, 1972.

^bS.B. Rai, B.R. Yadav, and D.K. Rai, "Perturbations in the $B^2\Sigma^+$ State of PO," J. Chim. Phys., Vol. 73, p. 905, 1976.

⁶M.A.A. Clyne and M.C. Heaven, "Laser-Induced Fluorescence of the PO Radical," Chem. Phys., Vol. 58, p. 145, 1981.

⁷K.C. Smyth and W.G. Mallard, "Two-Photon Ionization Processes of PO in a C_2H_2 /Air Flame," J. Chem. Phys., Vol. 77, p. 1779, 1982.

⁸J.S. Chou, D. Sumida, and C. Wittig, "2-Frequency 2-Photon Ionization of Nascent PO ($X^2\Pi$) from the Collision Free IR Photolysis of Dimethyl-Methylphosphonate," Chem. Phys. Lett., Vol. 100, p. 397, 1983.

⁹W.R. Anderson, S.W. Bunte, and A.J. Kotlar, "Laser-Excited Fluorescence of PO from Organophosphonate Esters," Conference on Lasers and Electro-Optics 83, Paper THD4, Baltimore, MD, May 1983.

structurally similar to nerve agents, either dimethyl-methylphosphonate [DMMP, $(\text{CH}_3\text{O})_2(\text{P}=\text{O})\text{CH}_3$] or its ethyl substituted analog, diethyl-ethylphosphonate (DEEP) which yielded comparable results. Excitation scans of the (0,0) band of the B-X system were obtained, similar to previous results.⁶ In addition, relative fluorescence intensity measurements were made for the vibrational progression emitted from the $v'=0$ excited level. Franck-Condon factors (FCFs) derived from these measurements are compared with values calculated from the RKR potentials. Though the nerve agents are violently poisonous, the simulants are only mildly toxic.* In fact, it is suggested that the simulants are safer and much more easily handled than the poisonous PO precursors used in previous studies.²⁻⁶

II. EXPERIMENTAL

PO was produced by flowing about 7×10^{-2} torr of DMMP or DEEP in about 1 torr of argon diluent through a 2450 MHz microwave discharge. The PO was excited downstream from the discharge in a stainless steel cell using radiation in the 3250Å region from a flashlamp pumped, tunable dye laser (Chromatix CMX-4). The laser linewidth was 0.3 cm^{-1} FWHM. Typical pulse energies were $\sim 0.2 \text{ mJ}$ with pulse duration $\sim 1 \text{ }\mu\text{sec}$. Fluorescence was detected using either a monochromator with photomultiplier tube or a photomultiplier tube with a visible cutoff filter. A small portion of the laser radiation was sampled by a reference photodiode prior to its entry into the fluorescence cell. Signals from the photomultiplier and power reference photodiode were processed, and their ratio was taken in a boxcar averager. Hard copy was obtained using a chart recorder or computer.

All of the figures and quantitative measurements presented herein involved DMMP as the precursor. However, as previously stated, qualitatively similar spectra were obtained using DEEP. Though careful quantitative studies were not performed using DEEP, the intensities of PO fluorescence from the two precursors were comparable indicating similar yields of PO for each.

III. RESULTS AND DISCUSSION

(0,0) Band Excitation Scans

The spectrum of PO was first identified by running excitation scans through the $(v', v'') = (0,0)$ region of the B-X system and comparing results to the previously measured emission^{2,3a} and LEF⁶ spectra. Since the spin-orbit constant of the X state is quite large (224 cm^{-1}),²⁻⁴ a large spectral splitting of the subbands from the $^2\Pi$ ground state is observed. Scans of both the $\text{B}^2\Sigma^+ + \text{X}^2\Pi_{1/2}$ and $\text{B}^2\Sigma^+ + \text{X}^2\Pi_{3/2}$ subbands are shown in Figure 1. The spectrum was obtained by scanning the laser wavelength while the monochromator remained fixed at 3250Å with a bandpass of 33Å FWHM. This bandpass encompassed nearly the entire (0,0) region so that results using the monochromator-photomultiplier vs filter-photomultiplier combinations were almost identical.

*Of course, one should not go out of one's way to ingest or breathe the simulants.

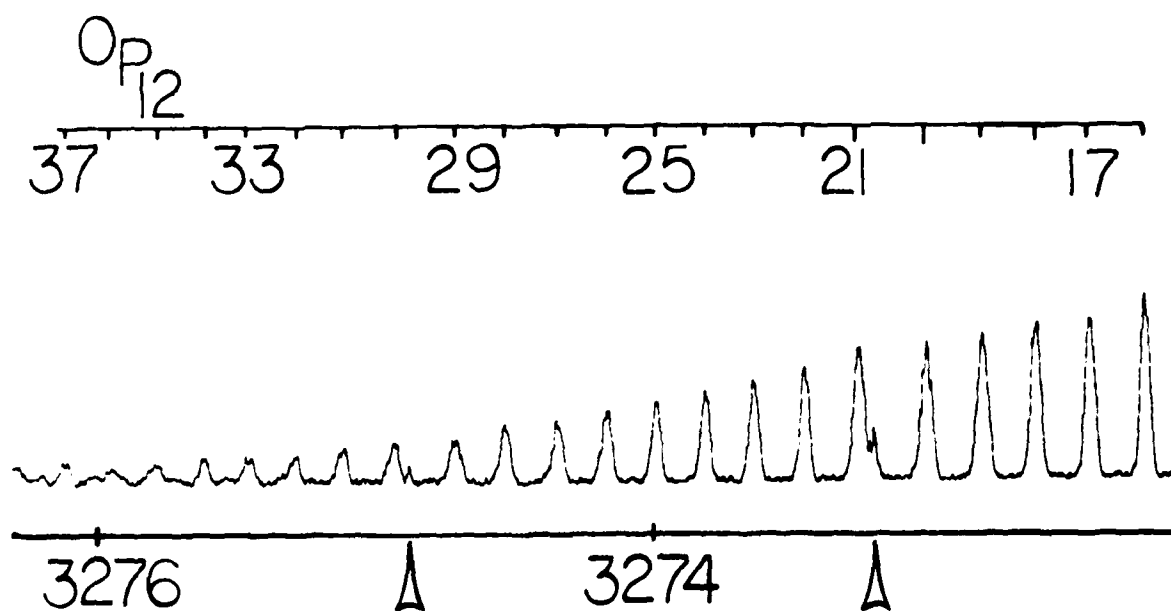


Figure 1a. A Laser Excitation Scan Through The (0,0) Band Of The $B^2\Sigma^+ + X^2\Pi$ System Of PO. Triangles On The Wavelength Scale Indicate Laser Etalon Reset Positions, An Artifact Of The Tuning Mechanism. A. The $B^2\Sigma^+ + X^2\Pi_{3/2}$ Subband. Wavelengths In Angstroms. (Continued)

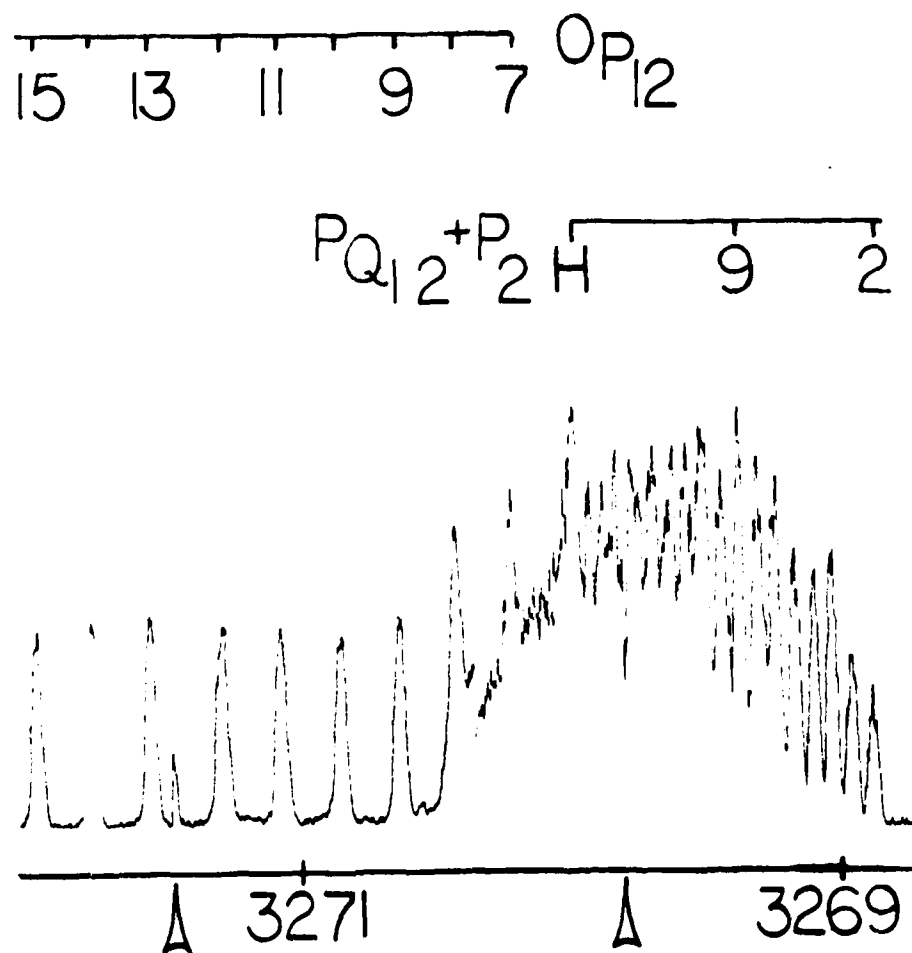


Figure 1a. A Laser Excitation Scan Through The (0,0) Band Of The $B^2\Sigma^+ + X^2\Pi$ System Of PO. Triangles On The Wavelength Scale Indicate Laser Etalon Reset Positions, An Artifact Of The Tuning Mechanism. A. The $B^2\Sigma^+ + X^2\Pi_{3/2}$ Subband.
Wavelengths In Angstroms. (Continued)

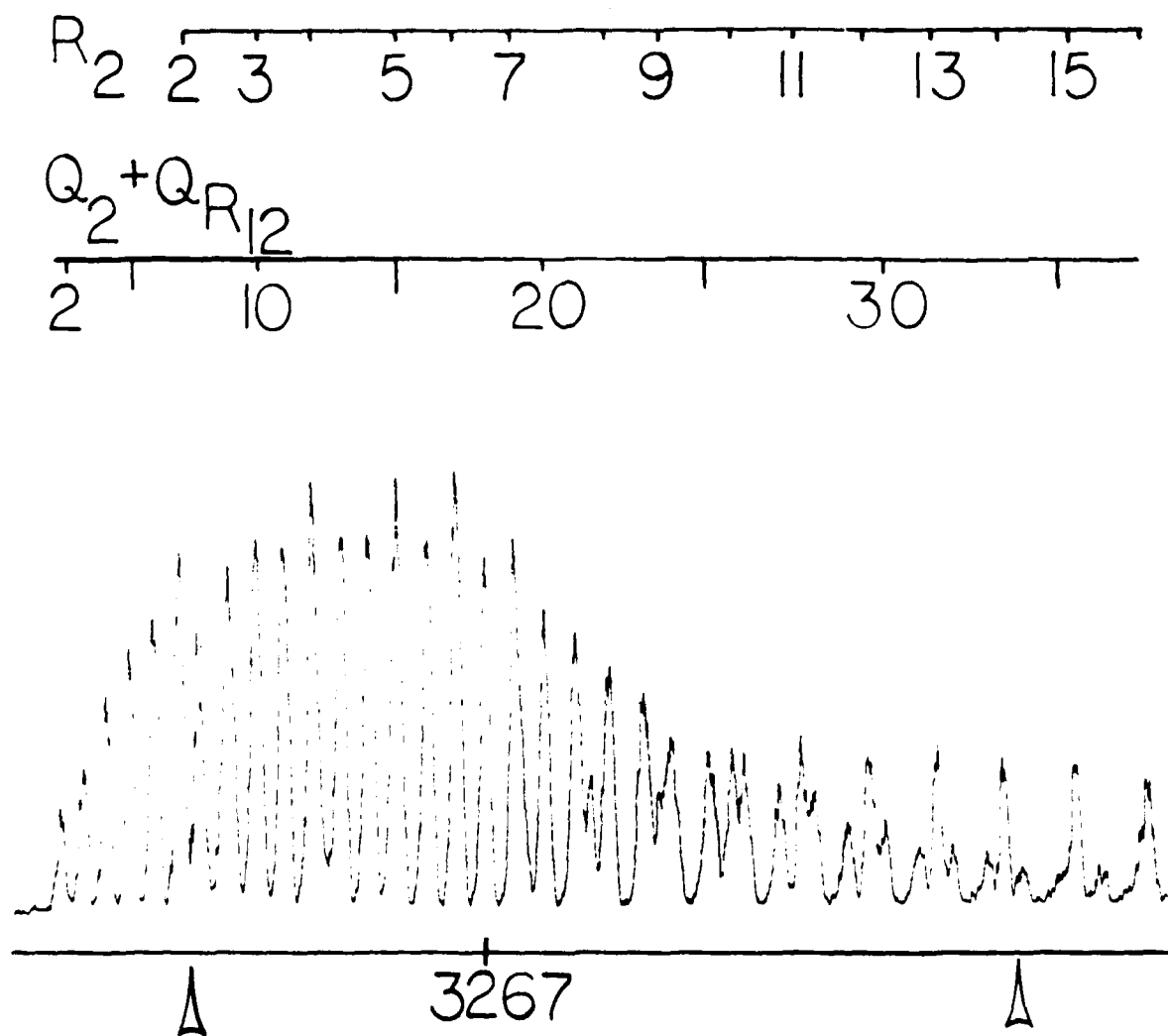


Figure 1a. A Laser Excitation Scan Through The (0,0) Band Of The $B^2\Sigma^+ + X^2\Pi$ System Of PO. Triangles On The Wavelength Scale Indicate Laser Etalon Reset Positions, An Artifact Of The Tuning Mechanism. A. The $B^2\Sigma^+ + X^2\Pi_{3/2}$ Subband. Wavelengths In Angstroms. (Continued)

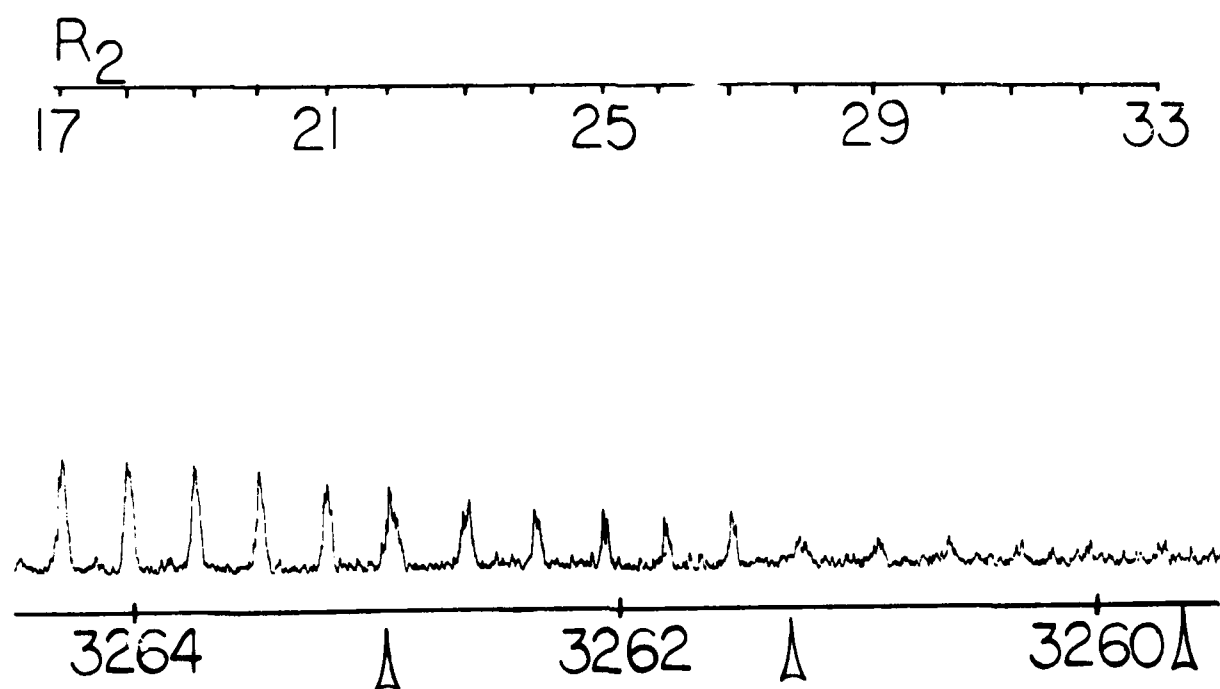


Figure 1a. A Laser Excitation Scan Through The (0,0) Band Of The $B^2\Sigma^+ + X^2\Pi$ System Of PO. Triangles On The Wavelength Scale Indicate Laser Etalon Reset Positions, An Artifact Of The **Tuning** Mechanism. A. The $B^2\Sigma^+ + X^2\Pi_{3/2}$ Subband.
Wavelengths In Angstroms.

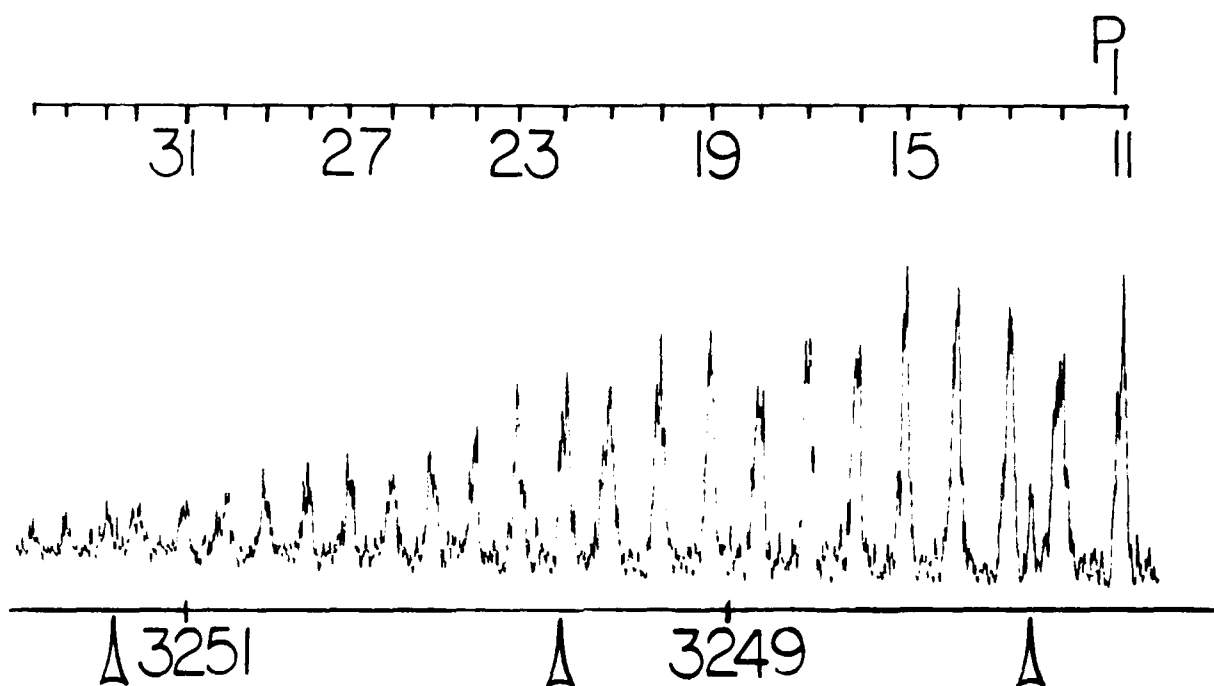


Figure 1b. A Laser Excitation Scan Through The (0,0) Band Of The $B^2\Sigma^+ + X^2\Pi$ System Of PO. Triangles On The Wavelength Scale Indicate Laser Etalon Reset Positions, An Artifact Of The Tuning Mechanism. B. The $B^2\Sigma^+ + X^2\Pi_{1/2}$ Subband. Wavelengths In Angstroms. The Q_1 Branch, From $N''=6$ To The Head, Was Recorded At A Sensitivity About Two Times Lower Than The Rest Of The Subband. (Continued)

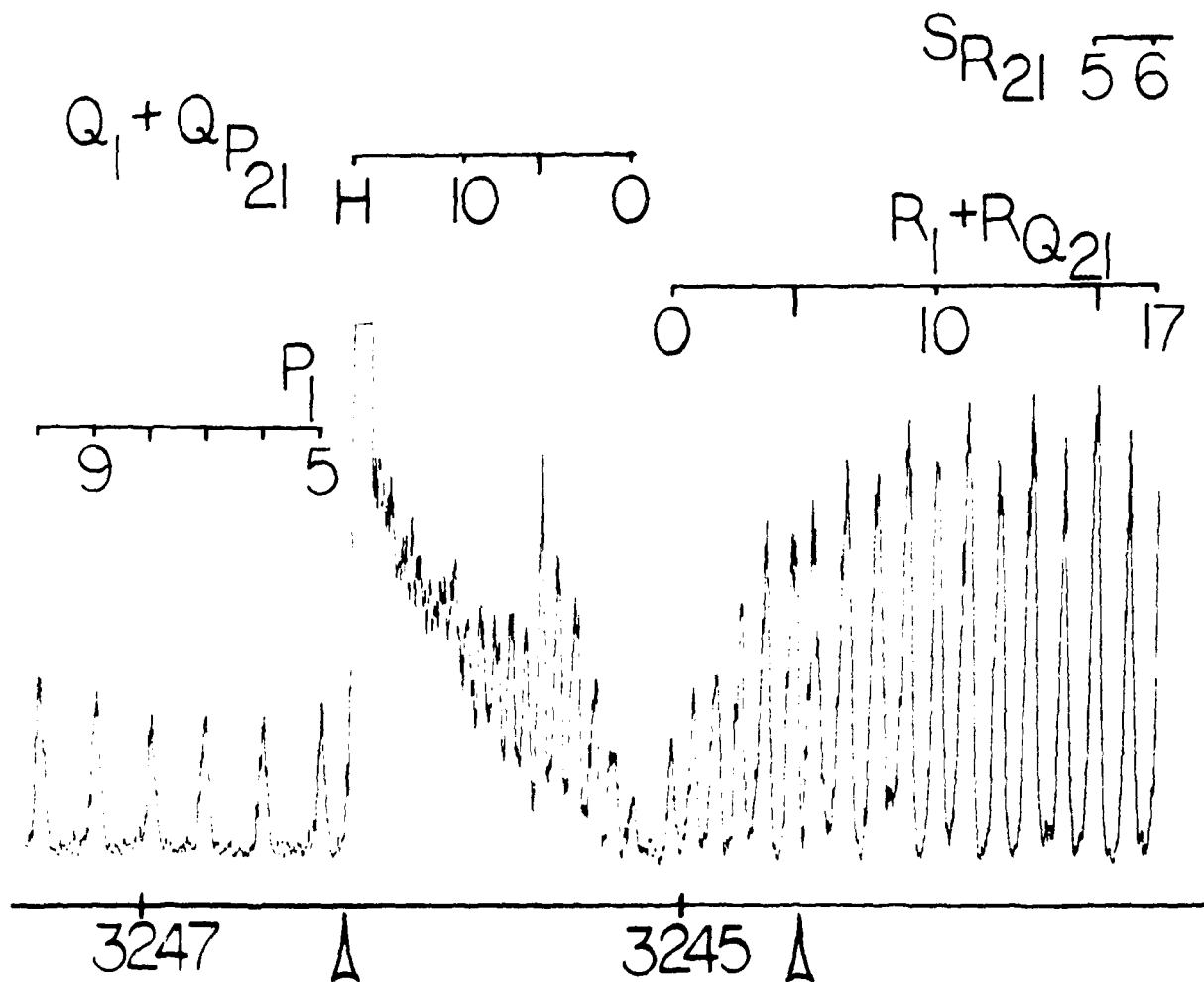


Figure 1b. A Laser Excitation Scan Through The (0,0) Band Of The $B^2\Sigma^+ + X^2\Pi$ System Of PO. Triangles On The Wavelength Scale Indicate Laser Etalon Reset Positions, An Artifact Of The Tuning Mechanism. B. The $B^2\Sigma^+ + X^2\Pi_{1/2}$ Subband. Wavelengths In Angstroms. The O_1 Branch, From $N''=6$ To The Head, Was Recorded At A Sensitivity About Two Times Lower Than The Rest Of The Subband. (Continued)

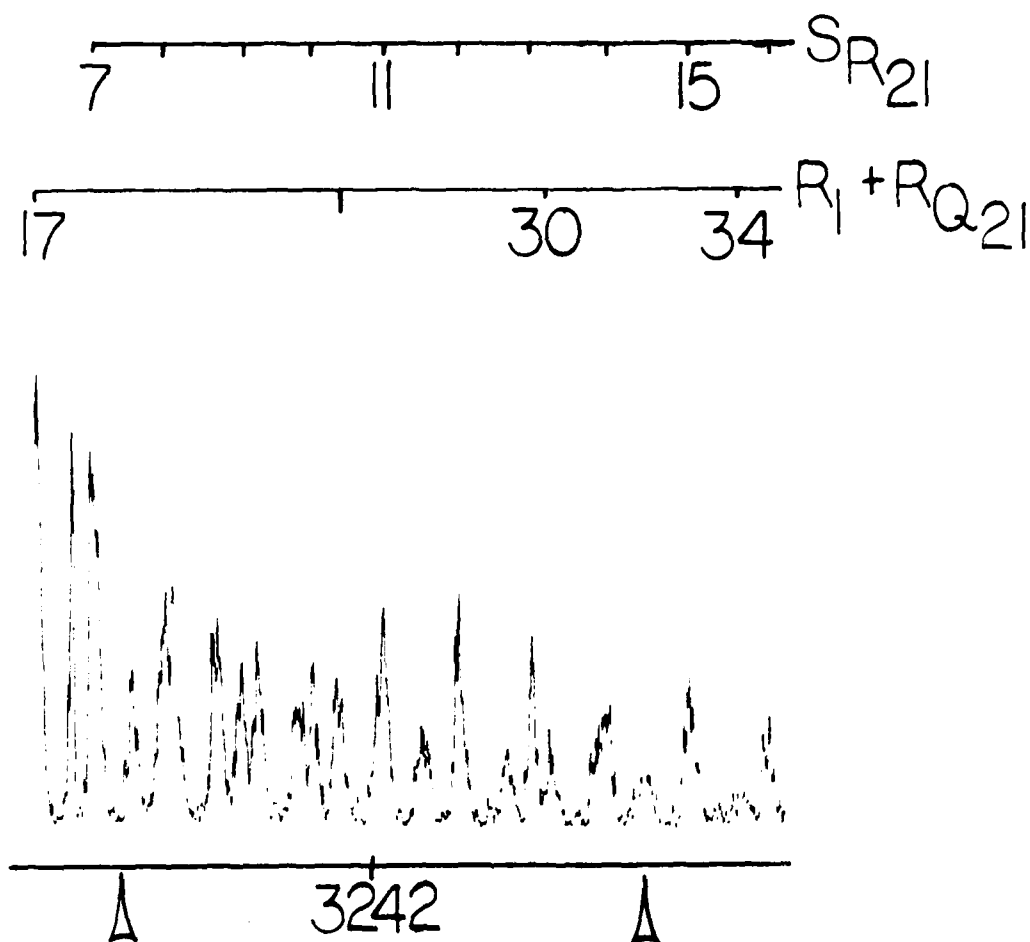


Figure 1b. A Laser Excitation Scan Through The (0,0) Band Of The $B^2\Sigma^+ + X^2\Pi$ System Of PO. Triangles On The Wavelength Scale Indicate Laser Etalon Reset Positions, An Artifact Of The Tuning Mechanism. B. The $B^2\Sigma^+ + X^2\Pi_{1/2}$ Subband. Wavelengths In Angstroms. The Q_1 Branch, From $N''=6$ To The Head, Was Recorded At A Sensitivity About Two Times Lower Than The Rest Of The Subband.

The earlier work on PO contains a discrepancy as to the rotational numbering of the P_1 branch in the (0,0) band.^{2,3,6} For this reason, the measured line positions were refitted¹⁰ using a weighted nonlinear least squares routine and standard doublet Hamiltonian.¹¹ The results indicate the original P_1 branch assignments^{2,3b} were correct.* Therefore, the rotational assignments in Refs. 2, 3b should be retained. The assignments of the P_1 branch in Figure 1, Reference 3a and Figure 2, Reference 6 should be increased by one unit.** The correct assignments are shown in our Figure 1b.

The fitting of the band has led to predicted bandhead positions and the corresponding values of J'' at which they occur. The J'' values at which the various branches turn have not appeared previously because of the difficulty in resolving this very dense region of the spectrum. The J'' value at which the branches reverse and the calculated wavelength of the appropriate transition are given in Table 1. The observed bandheads from Reference 3a are also given for comparison.

Franck-Condon Factors for $v'=0$

For the measurement of FCFs, the laser wavelength was fixed on the strongest feature of the excitation spectrum, the $Q_1 + Q_{P21}$ bandhead (see Figure 1 and Table 1). The monochromator was then scanned to obtain relative intensities of the vibrational bands originating from $v'=0$. Signals were obtained for $v''=0, 1$, and 2 , but not for $v''=3$. Since the FCFs are expected to

^{10a}A.J. Kotlar, "An Evaluation of the PO (0,0) $B^2\Sigma^+ - X^2\Pi_r$ Spectroscopic Parameters for Diagnostic Applications," Chemical Research and Development Center Scientific Conference on Chemical Defense Research, Aberdeen Proving Ground, MD, November 1983.

^bA.J. Kotlar, BRL Report to be published.

¹¹A.J. Kotlar, R.W. Field, J.I. Steinfeld, and J.A. Coxon, "Analysis of Perturbations in the $A^2\Pi - X^2\Sigma^+$ 'Red' System of CN," J. Mol. Spectrosc., Vol. 80, p. 86, 1980.

*The discrepancy apparently arose from an accidental mislabeling of the P_1 branch in Figure 1 of Reference 3a. Cross checks of our result by M. Heaven¹² and R.D. Verma¹³ were in agreement.

¹²M. Heaven, private communication.

¹³R.D. Verma, private communication.

** Some confusion could result because in the text of Reference 6, the authors state that the P_1 branch assignments of Singh² must be increased by one unit. However, in their Figure 2 of Reference 6, as in the similar Figure 1 of Reference 3a, the numbering is lowered by one unit. Therefore, we do indeed mean the numbering in their figure must be increased by one unit. It should be noted that the rotational assignments given in tabular form by Singhal^{3b} are in excellent agreement with those of Singh.

Table 1. Bandhead Positions in the (0,0) Band of the B-X System of PO^a

<u>Wavelength (Å)</u>		<u>Assignment</u>
<u>Observed</u>	<u>Calculated</u>	
3246.1	3246.2	Q ₁ (27.5)
	3246.2	Q _{P21} (27.5)
3270.4	3270.4	P ₂ (44.5)
	3270.5	P _{Q12} (45.5)

a - Observed values were taken from Reference 3a.

decrease for higher v'' , higher values were not checked. Magnitudes of the signal levels observed for $v''=0$ and 2 necessitated usage of different voltages (an uncalibrated gain change) on the photomultiplier. Therefore, the band intensity ratios were obtained in pairs with the (0,0):(0,1) ratio at low and the (0,1):(0,2) ratio at high sensitivity. At least four scans were obtained for each band at the necessary sensitivities. A representative pair of bands is shown in Figure 2. Areas under these curves were obtained by computer integration (trapezoidal summation) and averaged for the four runs. The area under the (0,0) bands was then corrected for a small amount of laser scatter from the cell walls and windows whose magnitude was obtained from runs with the microwave discharge off (see Figure 2). Finally, the combined lensing, monochromator-photomultiplier system's spectral sensitivity was calibrated using an NBS traceable tungsten standards lamp. The ratios of Einstein band emission coefficients thus obtained were $A_{0,1}:A_{0,0} = 0.0690 \pm 0.0073$ and $A_{0,2}:A_{0,1} = 0.0824 \pm 0.0119$. These ratios may be used irrespective of any assumptions about the electronic transition moment. If one assumes the electronic transition moment is constant over the range of internuclear distance sampled in the three vibrational bands, then by doing the appropriate algebraic manipulations, FCFs may be derived from these Einstein coefficient ratios. These are shown in Table 2.

Table 2. Measured and Calculated Franck-Condon Factors for the $v'=0$ Progression in the B-X System of PO. The electronic transition moment was assumed constant in the derivation of FCFs from experimental data (see text).

<u>(v', v'')</u>	<u>q_{v', v''} (meas.)</u>	<u>q_{v', v''} (RKR calc.)</u>
(0,0)	0.9213 \pm 0.0071	0.9776
(0,1)	0.0720 \pm 0.0076	0.0194
(0,2)	0.0067 \pm 0.0012	0.0028
(0,3)	Not detected	0.0001

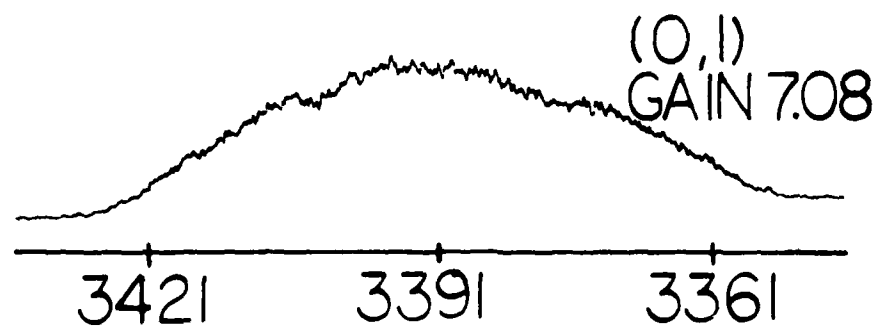
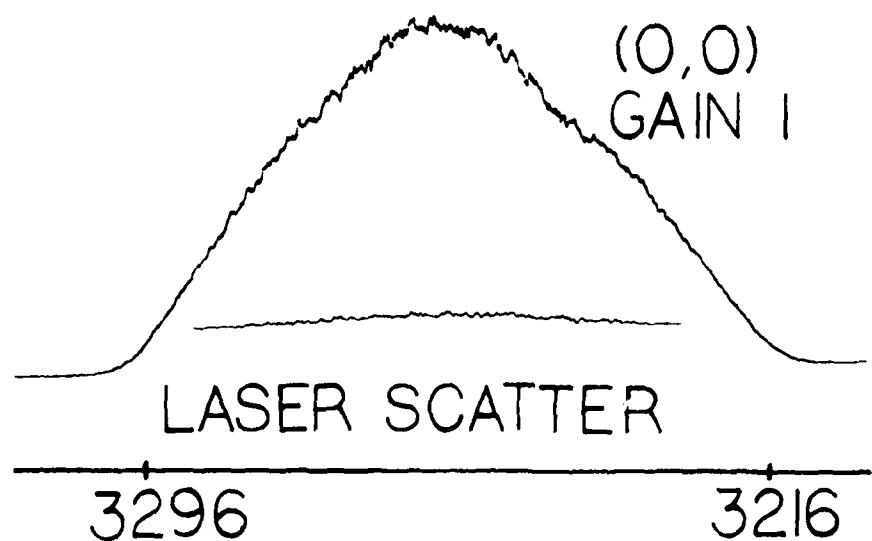


Figure 2. Fluorescence Scans Of The (0,0) And (0,1) Vibrational Bands. Wavelengths In Angstroms. Note That The Baseline For The Laser Scatter Scan Is Displaced Upwards From That For The Scan Of The (0,0) Band. The Scattering Correction To The (0,0) Intensity Is Actually Quite Small.

FCFs were also obtained from theoretical calculations for the entire v' , v'' array using the RKR potentials. Subsequent to these calculations, it was discovered that similar calculations had been performed previously by Singhal^{3b} and concurrently by Smyth and Mallard.⁷ All of these results are in excellent quantitative agreement for the $v'=0$ progression. The present theoretical results for the $v'=0$ progression are shown in Table 2 for comparison with the experimental results. Note that though the qualitative trends are quite similar, the quantitative agreement is poor, especially for the small FCFs. Small FCFs are especially difficult to calculate because they result from the cancellation of many positive and negative contributions in the integration of the vibrational wavefunctions; that is, they result essentially from the difference of two large, nearly equal numbers. Such problems have been suggested previously as the cause of a several orders of magnitude difference in measured and calculated FCFs in the A-X system of NH.¹⁴ Along these lines it is also worth noting that Smyth and Mallard state⁷ that their multiphoton ionization results could perhaps be better explained if the RKR calculational procedure underestimates several of the smaller FCFs. Unfortunately, the sketchy data presently available do not allow one to be certain whether problems with the FCF calculations or changes in the electronic transition moment with internuclear distance, as is known to occur in the A-X system of OH,¹⁵ are responsible for the poor agreement in Table 2. In any event, the Einstein emission coefficient ratios may be used irrespective of any assumptions about the form of the transition moment. The measured Einstein coefficients are to be preferred over those calculated from the theoretical FCFs, especially for rotational quanta near $N'=27$ (turning point of the Q_1 bandhead) where the measurements were performed.

Concentration of PO

A rough estimate of the density of PO in the excitation region was obtained using a procedure entirely analogous to that used previously for C_2 and CN,¹⁶ and NCO¹⁷ in a flame with changes appropriate to the tunable, pulsed laser. In the present work, the absolute fluorescence intensity in the (0,0) band was directly measured rather than referenced to N_2 Raman signals as was

¹⁴W.R. Anderson and D.R. Crosley, "Laser-Excited Fluorescence in the A-X System of NH," Chem. Phys. Lett., Vol. 62, p. 275, 1979.

^{15a}D.R. Crosley and R.K. Lengel, "Relative Transition Probabilities and the Electronic Transition Moment in the A-X System of OH," J. Quant. Spectrosc. Radiat. Transfer, Vol. 15, p. 579, 1975.

^bD.R. Crosley and R.K. Lengel, "Relative Transition Probabilities in the A-X System of OD," J. Quant. Spectrosc. Radiat. Transfer, Vol. 17, p. 59, 1977.

¹⁶J.A. Vanderhoff, R.A. Beyer, A.J. Kotlar, and W.R. Anderson, "Ar⁺ Laser-Excited Fluorescence of C_2 and CN Produced in a Flame," Combust. Flame, Vol. 49, p. 197, 1983.

¹⁷W.R. Anderson, J.A. Vanderhoff, A.J. Kotlar, M.A. DeWilde, and R.A. Beyer, "Intracavity Laser Excitation of NCO Fluorescence in an Atmospheric Pressure Flame," J. Chem. Phys., Vol. 77, p. 1677, 1982.

done previously. The Einstein coefficients were obtained using the B state lifetime, 250 nsec, measured in Reference 6 and the measured FCFs. Linestrengths necessary for the calculation of absorption coefficients for the resolved rotational lines were obtained using formulae of Earls.¹⁸ The pumping transition(s) was assumed to be Doppler broadened at 400 K, a temperature typical of our flow system. The measurement was made by pumping in the Q_1 bandhead where the laser line overlaps several rotational lines of PO. To estimate the effective number of transitions pumped, the relative intensities of $R_1(27)$ and the Q_1 bandhead, which occurs near $N''=27$, were obtained from the excitation scan. After correcting for rotational linestrengths, it was found that the laser effectively overlaps 6.9 transitions.* Finally, the importance of quenching was ascertained. It is expected that the quench rate of B state PO by Ar is certainly less than that of N_2 measured in the previous LEF study⁶ and found to be gas kinetic. Now, in comparing the Einstein emission coefficients, $A_{v,v''}$, to the quench rate, Q , for N_2 at 1 torr, it is found that the radiative and quench rates are nearly equal. Saturation checks were run using the ratioing boxcar averager so that stimulated emission is known to be unimportant. The fluorescence rate under these conditions is proportional to $A_{v,v''}/[(\sum_v A_{v,v''}) + Q]$ rather than $A_{v,v''}/Q$ as in Eq. (3) of Reference 16. The quench rate actually used was that of N_2 . However, if the quench rate of Ar is much less than for N_2 , the effect would reduce the estimated PO density by only a factor of about 2. The density estimated in this manner was about $1 \times 10^{10} \text{ cm}^{-3}$. Thus, about 1×10^{-5} of the phosphorus was present as PO. Because of the various uncertainties involved in these estimates, they are believed to be good only to within a factor of 10.**

IV. CONCLUSIONS

In these experiments, PO was obtained for fluorescence studies using organophosphonate esters as precursors. Discovery of these sources should aid in further research on PO as they are more easily handled than earlier precursors. The measurement of FCFs, together with the previous lifetime measurements, now makes quantitative determination of PO using absorption or fluorescence techniques possible.

¹⁸L.T. Earls, "Intensities in $2\pi - 2\Sigma$ Transitions in Diatomic Molecules," Physical Review, Vol. 48, p. 423, 1935.

*This procedure is valid because the Boltzmann fractions and normalized rotational linestrengths, and, hence, Einstein coefficients, do not vary significantly around $N''=27$. The result is similar to that obtained by dividing the laser linewidth, 0.3 cm^{-1} , by the density of lines in the region of the Q_1 bandhead.

**This uncertainty limit could have been reduced to about a factor of 2.5, even in the absence of further quench rate information, if a more careful laser power measurement had been available at the time of the experiment. The result shows that good quantitative measurements of PO could be made even in the absence of very precise quench rate information.

ACKNOWLEDGEMENTS

The authors extend their gratitude to Dr. M. Heaven and Dr. R.D. Verma for discussions of spectral assignments and to Dr. Verma for sending tabulated line positions used in early analysis of spectral data. Gratitude is also extended to Dr. Dennis Flanigan of the Chemical Research and Development Center for providing the organophosphonate esters used in this study. This study was performed under internal funds of the Ballistic Research Laboratory.

REFERENCES

1. References to earliest work may be found in Spectroscopic Data, Heteronuclear Diatomic Molecules, Vol. I, ed. S.N. Suchard, IFI/Plenum Data Company, NY, 1975. A compilation of papers from 1955 to 1979 is available in K.P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure, IV. Constants of Diatomic Molecules, Van Nostrand Reinhold, Co., NY, 1979.
2. N.L. Singh, "Rotational Analysis of the β Bands of Phosphorus Monoxide," Can. J. Phys., Vol. 37, p. 136, 1959.
- 3a. R.D. Verma and S.R. Singhal, "New Results on the $B^2\Sigma^+$, $b^4\Sigma^-$ and $X^2\Pi$ States of PO," Can. J. Phys., Vol. 53, p.411, 1975.
- b. S.R. Singhal, "High Resolution Study of the Spectral Region 3000Å - 3900Å of the PO Molecule," Ph.D. Thesis, University of New Brunswick, Fredericton, New Brunswick, Canada, 1973.
4. C. Couet, N. Tuan Anh, B. Coquart and H. Guenebaut, "Contribution A L'Etude Des Systemes Electroniques du Radical PO. 3^e Partie: Le Systeme β (transition $B^2\Sigma^+ - X^2\Pi$)," J. Chim. Phys., Vol. 65, p. 217, 1968.
- 5a. S.B. Rai, D.K. Rai, and K.N. Upadhyay, "Analysis of Some Bands of the β System of PO," J. Phys. B: Atom. Molec. Phys., Vol. 5, p. 1038, 1972.
- b. S.B. Rai, B.R. Yadav, and D.K. Rai, "Perturbations in the $B^2\Sigma^+$ State of PO," J. Chim. Phys., Vol. 73, p. 905, 1976.
6. M.A.A. Clyne and M.C. Heaven, "Laser-Induced Fluorescence of the PO Radical," Chem. Phys., Vol. 58, p. 145, 1981.
7. K.C. Smyth and W.G. Mallard, "Two-Photon Ionization Processes of PO in a C_2H_2 /Air Flame," J. Chem. Phys., Vol. 77, p. 1779, 1982.
8. J.S. Chou, D. Sumida, and C. Wittig, "2-Frequency 2-Photon Ionization of Nascent PO ($X^2\Pi$) from the Collision Free IR Photolysis of Dimethyl-Methylphosphonate," Chem. Phys. Lett., Vol. 100, p. 397, 1983.
9. W.R. Anderson, S.W. Bunte, and A.J. Kotlar, "Laser-Excited Fluorescence of PO from Organophosphonate Esters," Conference on Lasers and Electro-Optics 83, Paper THD4, Baltimore, MD, May 1983.
- 10a. A.J. Kotlar, "An Evaluation of the PO (0,0) $B^2\Sigma^+ - X^2\Pi_r$ Spectroscopic Parameters for Diagnostic Applications," Chemical Research and Development Center Scientific Conference on Chemical Defense Research, Aberdeen Proving Ground, MD, November 1983.
- b. A.J. Kotlar, BRL Report, to be published.
11. A.J. Kotlar, R.W. Field, J.I. Steinfeld, and J.A. Coxon, "Analysis of Perturbations in the $A^2\Pi - X^2\Sigma^+$ 'Red' System of CN," J. Mol. Spectrosc., Vol. 80, p. 86, 1980.

12. M. Heaven, private communication.
13. R.D. Verma, private communication.
14. W.R. Anderson and D.R. Crosley, "Laser-Excited Fluorescence in the A-X System of NH," Chem. Phys. Lett., Vol. 62, p. 275, 1979.
- 15a. D.R. Crosley and R.K. Lengel, "Relative Transition Probabilities and the Electronic Transition Moment in the A-X System of OH," J. Quant. Spectrosc. Radiat. Transfer, Vol. 15, p. 579, 1975.
- b. D.R. Crosley and R.K. Lengel, "Relative Transition Probabilities in the A-X System of OD," J. Quant. Spectrosc. Radiat. Transfer, Vol. 17, p. 59, 1977.
16. J.A. Vanderhoff, R.A. Beyer, A.J. Kotlar, and W.R. Anderson, "Ar⁺ Laser-Excited Fluorescence of C₂ and CN Produced in a Flame," Combust. Flame, Vol. 49, p. 197, 1983.
17. W.R. Anderson, J.A. Vanderhoff, A.J. Kotlar, M.A. DeWilde, and R.A. Beyer, "Intracavity Laser Excitation of NCO Fluorescence in an Atmospheric Pressure Flame," J. Chem. Phys., Vol. 77, p. 1677, 1982.
18. L.T. Earls, "Intensities in $2\Pi - 2\Sigma$ Transitions in Diatomic Molecules," Physical Review, Vol. 48, p. 423, 1935.

DISTRIBUTION LIST

<u>No. Of Copies</u>	<u>Organization</u>	<u>No. Of Copies</u>	<u>Organization</u>
12	Administrator Defense Technical Info Center ATTN: DTIC-DDA Cameron Station Alexandria, VA 22314	1	Director USA Air Mobility Research and Development Laboratory Ames Research Center Moffett Field, CA 94035
1	HQ DA DAMA-ART-M Washington, DC 20310	4	Commander US Army Research Office ATTN: R. Ghirardelli D. Mann R. Singleton R. Shaw Research Triangle Park, NC 27709
1	Commander US Army Materiel Command ATTN: AMCDRA-ST 5001 Eisenhower Avenue Alexandria, VA 22333	1	Commander USA Communications- Electronics Command ATTN: AMSEL-ED Fort Monmouth, NJ 07703
1	Commander Armament R&D Center USA AMCCOM ATTN: SMCAR-TDC Dover, NJ 07801	1	Commander USA Electronics Research and Development Command Technical Support Activity ATTN: DELSD-L Fort Monmouth, NJ 07703
1	Commander Armament R&D Center USA AMCCOM ATTN: SMCAR-TSS Dover, NJ 07801-5001	2	Commander USA AMCCOM, ARDC ATTN: SMCAR-LCA-G D.S. Downs J.A. Lannon Dover, NJ 07801
1	Commander USA AMCCOM ATTN: SMCAR-ESP-L Rock Island, IL 61299	1	Commander USA AMCCOM, ARDC ATTN: SMCAR-LC, L. Harris Dover, NJ 07801
1	Director Benet Weapons Laboratory Armament R&D Center USA AMCCOM ATTN: SMCAR-ICB-TL Watervliet, NY 12189	1	Commander USA AMCCOM, ARDC ATTN: SMCAR-SCA-T L. Stiefel Dover, NJ 07801
1	Commander USA Aviation Research and Development Command ATTN: AMSAV-E 4300 Goodfellow Blvd. St. Louis, MO 63120	1	Air Force Armament Lab ATTN: AFATL/DLODL Eglin AFB, FL 32542-5000

DISTRIBUTION LIST

<u>No. Of Copies</u>	<u>Organization</u>	<u>No. Of Copies</u>	<u>Organization</u>
1	Commander USA Missile Command ATTN: AMSMI-R Redstone Arsenal, AL 35898	1	Commander Naval Air Systems Command ATTN: J. Ramnarace, AIR-54111C Washington, DC 20360
1	Commander USA Missile Command ATTN: AMSMI-YDL Redstone Arsenal, AL 35898	3	Commander Naval Ordnance Station ATTN: C. Irish S. Mitchell P.L. Stang, Code 515 Indian Head, MD 20640
2	Commander USA Missile Command ATTN: AMSMI-RK, D.J. Ifshin Redstone Arsenal, AL 35898	1	Commander Naval Surface Weapons Center ATTN: J.L. East, Jr., G-20 Dahlgren, VA 22448
1	Commander USA Tank Automotive Command ATTN: AMSTA-TSL Warren, MI 48090	2	Commander Naval Surface Weapons Center ATTN: R. Bernecker, R-13 G.B. Wilmot, R-16 Silver Spring, MD 20910
1	Director USA TRADOC Systems Analysis Activity ATTN: ATAA-SL WSMR, NM 88002	4	Commander Naval Weapons Center ATTN: R.L. Derr, Code 389 China Lake, CA 93555
1	Commandant US Army Infantry School ATTN: ATSH-CD-CSO-OR Fort Benning, GA 31905	2	Commander Naval Weapons Center ATTN: Code 3891, T. Boggs K.J. Graham China Lake, CA 93555
1	Commander USA Army Development and Employment Agency ATTN: MODE-TED-SAB Fort Lewis, WA 98433	5	Commander Naval Research Laboratory ATTN: L. Harvey J. McDonald E. Oran J. Shnur R.J. Doyle, Code 6110 Washington, DC 20375
1	Office of Naval Research Department of the Navy ATTN: R.S. Miller, Code 432 800 N. Quincy Street Arlington, VA 22217	1	Commanding Officer Naval Underwater Systems Center Weapons Dept. ATTN: R.S. Lazar/Code 36301 Newport, RI 02840
1	Navy Strategic Systems Project Office ATTN: R.D. Kinert, SP 2731 Washington, DC 20376		

DISTRIBUTION LIST

<u>No. Of</u> <u>Copies</u>	<u>Organization</u>	<u>No. Of</u> <u>Copies</u>	<u>Organization</u>
1	Superintendent Naval Postgraduate School Dept. of Aeronautics ATTN: D.W. Netzer Monterey, CA 93940	2	Atlantic Research Corp. ATTN: M.K. King 5390 Cherokee Avenue Alexandria, VA 22314
5	AFRPL (DRSC) ATTN: R. Geisler D. George D. Weaver J. Levine W. Roe Edwards AFB, CA 93523	1	Atlantic Research Corp. ATTN: R.H.W. Waesche 7511 Wellington Road Gainesville, VA 22065
		1	AVCO Everett Rsch. Lab. Div. ATTN: D. Stickler 2385 Revere Beach Parkway Everett, MA 02149
		1	Battelle Memorial Institute Tactical Technology Center ATTN: J. Huggins 505 King Avenue Columbus, OH 43201
2	AFOSR ATTN: L.H. Caveny J.M. Tishkoff Bolling Air Force Base Washington, DC 20332	2	Exxon Research & Eng. Co. ATTN: A. Dean M. Chou P.O. Box 45 Linden, NJ 07036
1	AFWL/SUL Kirtland AFB, NM 87117		
1	NASA Langley Research Center ATTN: G.B. Northam/MS 168 Hampton, VA 23365	1	Ford Aerospace and Communications Corp. DIVAD Division Div. Hq., Irvine ATTN: D. Williams Main Street & Ford Road Newport Beach, CA 92663
4	National Bureau of Standards ATTN: J. Hastie M. Jacox T. Kashiwagi H. Semerjian US Department of Commerce Washington, DC 20234	1	General Electric Armament & Electrical Systems ATTN: M.J. Bulman Lakeside Avenue Burlington, VT 05401
1	Aerojet Solid Propulsion Co. ATTN: P. Micheli Sacramento, CA 95813	1	General Electric Company ATTN: M. Lapp Schenectady, NY 12301
1	Applied Combustion Technology, Inc. ATTN: A.M. Varney P.O. Box 17885 Orlando, FL 32860		

DISTRIBUTION LIST

<u>No. Of Copies</u>	<u>Organization</u>	<u>No. Of Copies</u>	<u>Organization</u>
1	General Motors Rsch Labs Physics Department ATTN: R. Teets Warren, MI 48090	1	Los Alamos National Lab ATTN: B. Nichols T7, MS-B284 P.O. Box 1663 Los Alamos, NM 87545
3	Hercules, Inc. Alleghany Ballistics Lab. ATTN: R.R. Miller P.O. Box 210 Cumberland, MD 21501	1	Olin Corporation Smokeless Powder Operations ATTN: R.L. Cook P.O. Box 222 St. Marks, FL 32355
3	Hercules, Inc. Bacchus Works ATTN: K.P. McCarty P.O. Box 98 Magna, UT 84044	1	Paul Gough Associates, Inc. ATTN: P.S. Gough 1048 South Street Portsmouth, NH 03801
1	Hercules, Inc. AFATL/DLDBL ATTN: R.L. Simmons Eglin AFB, FL 32542	2	Princeton Combustion Research Laboratories, Inc. ATTN: M. Summerfield N.A. Messina 475 US Highway One Monmouth Junction, NJ 08852
1	Honeywell, Inc. Defense Systems Division ATTN: D.E. Broden/ MS MN50-2000 600 2nd Street NE Hopkins, MN 55343	1	Hughes Aircraft Company ATTN: T.E. Ward 8433 Fallbrook Avenue Canoga Park, CA 91303
1	IBM Corporation ATTN: A.C. Tam Research Division 5600 Cottle Road San Jose, CA 95193	1	Rockwell International Corp. Rocketdyne Division ATTN: J.E. Flanagan/HB02 6633 Canoga Avenue Canoga Park, CA 91304
1	Director Lawrence Livermore National Laboratory ATTN: C. Westbrook Livermore, CA 94550	3	Sandia National Laboratory Combustion Sciences Dept. ATTN: R. Cattolica D. Stephenson P. Mattern Livermore, CA 94550
1	Lockheed Missiles & Space Co. ATTN: George Lo 3251 Hanover Street Dept. 52-35/B204/2 Palo Alto, CA 94304	1	Sandia National Laboratory ATTN: M. Smooke Division 8353 Livermore, CA 94550
		1	Science Applications, Inc. ATTN: R.B. Edelman 23146 Cumorah Crest Woodland Hills, CA 91364

DISTRIBUTION LIST

<u>No. Of Copies</u>	<u>Organization</u>	<u>No. Of Copies</u>	<u>Organization</u>
1	Science Applications, Inc. ATTN: H.S. Pergament 1100 State Road, Bldg. N Princeton, NJ 08540	2	United Technologies Corp. ATTN: R.S. Brown R.O. McLaren P.O. Box 358 Sunnyvale, CA 94086
4	SRI International ATTN: S. Barker D. Crosley D. Golden Tech Lib 333 Ravenswood Avenue Menlo Park, CA 94025	1	Universal Propulsion Company ATTN: H.J. McSpadden Black Canyon Stage 1 Box 1140 Phoenix, AZ 85029
1	Stevens Institute of Tech. Davidson Laboratory ATTN: R. McAlevy, III Hoboken, NJ 07030	1	Veritay Technology, Inc. ATTN: E.B. Fisher P.O. Box 22 Bowmansville, NY 14026
1	Teledyne McCormack-Selph ATTN: C. Leveritt 3601 Union Road Hollister, CA 95023	1	Brigham Young University Dept. of Chemical Engineering ATTN: M.W. Beckstead Provo, UT 84601
1	Thiokol Corporation Elkton Division ATTN: W.N. Brundige P.O. Box 241 Elkton, MD 21921	1	California Institute of Tech. Jet Propulsion Laboratory ATTN: MS 125/159 4800 Oak Grove Drive Pasadena, CA 91103
3	Thiokol Corporation Huntsville Division ATTN: D.A. Flanagan Huntsville, AL 35807	1	California Institute of Technology ATTN: F.E.C. Culick/ MC 301-46 204 Karman Lab. Pasadena, CA 91125
3	Thiokol Corporation Wasatch Division ATTN: J.A. Peterson P.O. Box 524 Brigham City, UT 84302	1	University of California, Berkeley Mechanical Engineering Dept. ATTN: J. Daily Berkeley, CA 94720
1	United Technologies ATTN: A.C. Eckbreth East Hartford, CT 06108	1	University of California Los Alamos National Lab. ATTN: T.D. Butler P.O. Box 1663, Mail Stop B216 Los Alamos, NM 87545

DISTRIBUTION LIST

<u>No. Of Copies</u>	<u>Organization</u>	<u>No. Of Copies</u>	<u>Organization</u>
2	University of California, Santa Barbara Quantum Institute ATTN: K. Schofield M. Steinberg Santa Barbara, CA 93106	1	University of Illinois Dept. of Mech./Indust Engr ATTN: H. Krier 144MEB, 1206 W. Green St. Urbana, IL 61801
1	University of Southern California Dept. of Chemistry ATTN: S. Benson Los Angeles, CA 90007	1	Johns Hopkins University/APL Chemical Propulsion Information Agency ATTN: T.W. Christian Johns Hopkins Road Laurel, MD 20707
1	Case Western Reserve Univ. Div. of Aerospace Sciences ATTN: J. Tien Cleveland, OH 44135	1	University of Minnesota Dept. of Mechanical Engineering ATTN: E. Fletcher Minneapolis, MN 55455
1	Cornell University Department of Chemistry ATTN: E. Grant Baker Laboratory Ithaca, NY 14853	4	Pennsylvania State University Applied Research Laboratory ATTN: G.M. Faeth K.K. Kuo H. Palmer M. Micci University Park, PA 16802
1	Univ. of Dayton Rsch Inst. ATTN: D. Campbell AFRPL/PAP Stop 24 Edwards AFB, CA 93523	1	Polytechnic Institute of NY ATTN: S. Lederman Route 110 Farmingdale, NY 11735
1	University of Florida Dept. of Chemistry ATTN: J. Winefordner Gainesville, FL 32611	2	Princeton University Forrestal Campus Library ATTN: K. Brezinsky I. Glassman P.O. Box 710 Princeton, NJ 08540
3	Georgia Institute of Technology School of Aerospace Engineering ATTN: E. Price Atlanta, GA 30332	1	Princeton University MAE Dept. ATTN: F.A. Williams Princeton, NJ 08544
2	Georgia Institute of Technology School of Aerospace Engineering ATTN: W.C. Strahle B.T. Zinn Atlanta, GA 30332		

DISTRIBUTION LIST

<u>No. Of Copies</u>	<u>Organization</u>	<u>No. Of Copies</u>	<u>Organization</u>
2	Purdue University School of Aeronautics and Astronautics ATTN: R. Glick J.R. Osborn Grissom Hall West Lafayette, IN 47906	1	Virginia Polytechnic Institute and State University ATTN: J.A. Schetz Blacksburg, VA 24061
			<u>Aberdeen Proving Ground</u>
3	Purdue University School of Mechanical Engineering ATTN: N.M. Laurendeau S.N.B. Murthy D. Sweeney TSPC Chaffee Hall West Lafayette, IN 47906		Dir, USAMSAA ATTN: AMXSY-D AMXSY-MP, H. Cohen Cdr, USATECOM ATTN: AMSTE-TO-F Cdr, CRDC, AMCCOM ATTN: SMCCR-RSP-A SMCCR-MU SMCCR-SPS-IL SMCCR-RSP-R, L. Hoffland SMCCR-RSP-R, S. Christesen (2 copies) SMCCR-RSP-PS, E. Stuebing
1	Rensselaer Polytechnic Inst. Dept. of Chemical Engineering ATTN: A. Fontijn Troy, NY 12181		
2	Southwest Research Institute ATTN: R.E. White A.B. Wenzel 8500 Culebra Road San Antonio, TX 78228		
1	Stanford University Dept. of Mechanical Engineering ATTN: R. Hanson Stanford, CA 94305		
1	University of Texas Dept. of Chemistry ATTN: W. Gardiner Austin, TX 78712		
1	University of Utah Dept. of Chemical Engineering ATTN: G. Flandro Salt Lake City, UT 84112		

USER EVALUATION SHEET/CHANGE OF ADDRESS

This Laboratory undertakes a continuing effort to improve the quality of the reports it publishes. Your comments/answers to the items/questions below will aid us in our efforts.

1. BRL Report Number _____ Date of Report _____

2. Date Report Received _____

3. Does this report satisfy a need? (Comment on purpose, related project, or other area of interest for which the report will be used.) _____

4. How specifically, is the report being used? (Information source, design data, procedure, source of ideas, etc.) _____

5. Has the information in this report led to any quantitative savings as far as man-hours or dollars saved, operating costs avoided or efficiencies achieved, etc? If so, please elaborate. _____

6. General Comments. What do you think should be changed to improve future reports? (Indicate changes to organization, technical content, format, etc.) _____

CURRENT
ADDRESS

Name _____
Organization _____
Address _____
City, State, Zip _____

7. If indicating a Change of Address or Address Correction, please provide the New or Correct Address in Block 6 above and the Old or Incorrect address below.

OLD
ADDRESS

Name _____
Organization _____
Address _____
City, State, Zip _____

(Remove this sheet along the perforation, fold as indicated, staple or tape closed, and mail.)

----- FOLD HERE -----

Director
US Army Ballistic Research Laboratory
ATTN: AMXBR-OD-ST
Aberdeen Proving Ground, MD 21005-5066

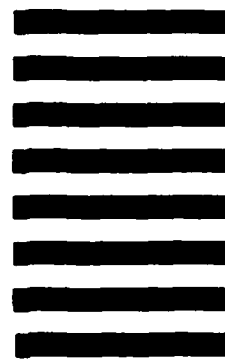


NO POSTAGE
NECESSARY
IF MAILED
IN THE
UNITED STATES

OFFICIAL BUSINESS
PENALTY FOR PRIVATE USE, \$300

BUSINESS REPLY MAIL
FIRST CLASS PERMIT NO 12062 WASHINGTON, DC
POSTAGE WILL BE PAID BY DEPARTMENT OF THE ARMY

Director
US Army Ballistic Research Laboratory
ATTN: AMXBR-OD-ST
Aberdeen Proving Ground, MD 21005-9989



----- FOLD HERE -----

END

FILMED

5-85

DTIC